



Review

Perovskite-type mixed oxides as catalytic material for NO removal

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ABSTRACT

Perovskite-type mixed oxides, with ABO_3 or A_2BO_4 structure, are promising materials as catalysts for NO removal due to their low cost, high thermal stability and of course, good catalytic performances. Their unique structural properties (e.g. A- and B-site cations could be replaced by a foreign one without destroying the matrix structure) make it possible to study the correlations between structure properties and catalytic performances. In this work the effects of solid-state and electrochemical properties of perovskite-type catalyst on NO removal activity is reviewed. Also, current experiments regarding the catalytically active site and the reaction mechanism of NO removal on perovskite-type mixed oxides are compared and discussed.

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1. Introduction

Catalytic removal of nitrogen oxide (NO) is a mature but still challenging task in environmental catalysis, owing to the fact that it is causing serious damages to the environment, climate and to human health [1]; nitrogen oxides are one of the most significant components of the exhausts from the high-temperature combustion process of fossil fuels. These nitrogen oxides, mainly emitted from vehicles or industrial plants lead to high local ozone concentrations and to acid rain [2]. Although the reaction of nitrogen oxide to nitrogen and oxygen ($\text{NO} = 1/2\text{N}_2 + 1/2\text{O}_2$) is thermodynamically favored it is kinetically hindered, and hence a

catalyst is needed for the decomposition of NO [3]. However, a catalyst which combines high-efficiency for NO removal with low manufacturing cost is still searched for. The search for an efficient catalyst becomes even more urgent as more strict regulations on exhausts emission issued in the recent years.

Currently, two technologies are proposed for NO removal in catalysis: NO reduction and NO decomposition. The former requires the addition of a supplemental reductant which however causes further problems, such as higher equipment cost, harsher reaction conditions and secondary pollution. Alternatively, NO decomposition is of high interest since no additional reactant is required and the products are exclusively composed out of N_2 and O_2 . Although the route of NO decomposition encounters more serious problems in practice, especially the low reaction rate, it still receives great interest because it can be regarded as a “green” process.

A review on the literature shows that the main catalytic systems applied in NO removal are the following three systems: M-ZSM-5

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zeolites (M: Transitional metal) [4,5], noble metals [6,7], and composite mixed oxides [8–16]. However, the first, ZSM-5, possess low hydrothermal stability while the second, noble metals, are costly and prone to aggregation. Thus composite mixed oxides, mostly with perovskite-type structure (ABO_3 or A_2BO_4), can be seen as interesting alternatives as they are low-cost materials and stable even at above 1000 °C. Thus, from the standpoint of the catalyst lifetime (structural stability) and the catalyst manufacturing cost, which are two important criterions for industrial catalyst, perovskite-type mixed oxides could be a potential candidate for NO removal.

Furthermore, some structural features of perovskite-type oxides make them interesting materials for investigation in catalysis [17]: (1) the defined structure, which allows the introduction of various metal ions to its structural framework; (2) the cation at both A- and B-site could be substituted by a foreign one without destroying the matrix structure, which allows the controlled alternation of the oxidation state of cations or the creation of oxygen vacancies; (3) through substitution a relationship between physiochemical properties and catalytic performances could be plotted, which allows a better insight into structure-property relationships and into the reaction mechanism.

This paper intends to review the catalytic NO removal on perovskite-type catalysts. For a general review about catalytic NO removal, and the chemical structure and performances of perovskite-type oxides we would like to refer the reader to the literature [2,18]. So far, this review concentrates mainly on the following six topics: (i) A brief description of perovskite-type oxides; (ii) The effect of A-site substitution; (iii) The effect of B-site substitution; (iv) Perovskite-type oxides as catalyst or catalyst support; (v) The relationships between electrochemical properties and catalytic performances and; (vi) The active site structure and reaction mechanism.

2. A brief description of perovskite-type oxides

The “perovskite-type catalyst” mentioned here, if not further specified, refers to the oxides with ABO_3 and/or A_2BO_4 structure, as shown in Fig. 1. Here, A is a larger cation that locates on the edge of the structure, B is a smaller cation locating in the center of the octahedron.

In the structure, A- and/or B-site cations could be replaced by a foreign one without destroying the matrix structure, as marked by a red cycle (for A' cation) in Fig. 1. Depending on the oxidation state of A'-site cation, oxygen vacancy (represented by a blue sign “■” in

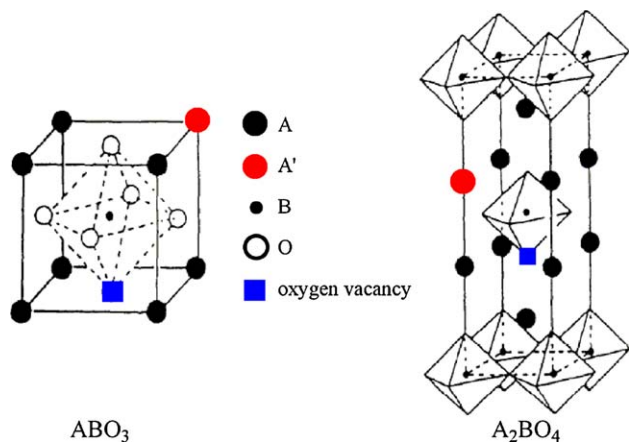


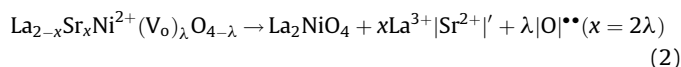
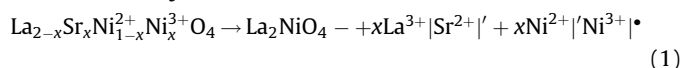
Fig. 1. Ideal models of perovskite-type oxides with ABO_3 and A_2BO_4 structure. The red circle means that an A-site cation was substituted by a foreign one; the blue square represents an oxygen vacancy. Note: the oxygen symbol was not shown in the A_2BO_4 structure for simplification.

Fig. 1) could be created in order to keep the oxides in an electro neutral state (Note: the change of B-site cation was not exemplified here for simplification).

Of course, the above stated does not mean that the A-site cation could be replaced freely with another one with random ion radius and quantity, because the substitution of cations will cause a deviation of the structure from the ideal one. All of the ions in the structure should satisfy the requirement of tolerance factor (t) of perovskite-type oxides as introduced by Goldschmidt [19], in form of $t = (r_A + r_O) / \{\sqrt{2}(r_B + r_O)\}$, where t is in the range of 0.75–1.0.

3. Effect of A-site substitution

It has been reported that for perovskite-type catalysts, the larger A-site cation is catalytically inactive, and that substitution of A-site cations therefore just affects the oxidation state of the B-site cations and/or creates non-stoichiometric oxygen [20]. For example, the substitution of La^{3+} cations in La_2NiO_4 with cations with lower valence, e.g. Sr^{2+} , leads to the increase of the oxidation state of B-site cations, for example from Ni^{2+} to Ni^{3+} , or the creation of an oxygen vacancy (V_O), or both in order to keep the electroneutrality, as shown below:



Therefore, if the foreign A'-site cation can not change its oxidation state (in this example Sr^{2+}), the effect of A-site substitution on the catalytic performance is an indirect one, i.e., by changing the oxidation state of B-site cation or by creating an oxygen vacancy. This is illustrated in Fig. 2, where the effect of Sr substitution for La on the oxidation state of the B-site ion, the amount of non-stoichiometric oxygen and the catalytic performance of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ is shown. It is seen that the activity of NO decomposition increased at the beginning, but then decreased with further substitution of Sr^{2+} for La^{3+} , and the best activity is found at $x = 0.6$, where obviously the average oxidation state of B-site cation is altered and the oxygen vacancy is created. This indicates that although Sr^{2+} is not active for NO decomposition, it could affect the reaction rate through changing the average oxidation of B-site cation and/or creating an oxygen vacancy. The highest activity observed at sample $x = 0.6$ is due to the suitable transformation of $\text{Ni}^{2+}/\text{Ni}^{3+}$ couple as described in the literature [21]. This means that for NO decomposition, a higher oxidation state of the B-site cation is not suitable and the existence of an oxygen vacancy is necessary.

In fact, this indirect influence of A-site substitution has already been noticed and discussed in previous literatures. Yasuda et al. [22] investigated the effect of Sr substitution on the catalytic performance of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ for NO decomposition, and concluded that the substitution effect is caused by changing the average oxidation state of copper. The plot in Fig. 3 shows that the activity indeed has a close relation to the average oxidation state of copper, whose value depends closely on the amount of Sr^{2+} substitution.

Recently, barium was considered as a promising A-site ion of perovskite-type catalyst for NO removal, because not only of its low oxidation state (+2), but also for its potential ability to trap NO_x , which ensures the supply of NO_x species to the reaction. A recent work [23] on the Ba substitution indicated that at $x = 0.8$ in $\text{La}_{2-x}\text{Ba}_x\text{NiO}_4$ showed the best activity for NO decomposition (see Fig. 4a), which is mostly due to the existence of BaCO_3 phase in the catalyst. Following investigation on the catalyst by NO_2 -TPD

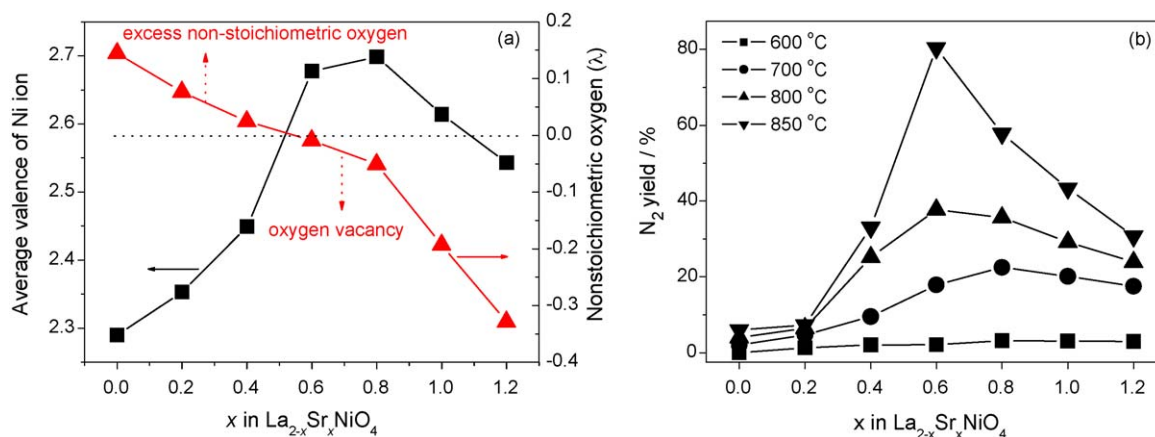


Fig. 2. (a) Dependence of average valence of Ni ion and non-stoichiometric oxygen (λ) on the Sr content (x) in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\lambda}$; (b) N_2 yield obtained from the NO decomposition reaction carried out on $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\lambda}$ at different temperatures [21].

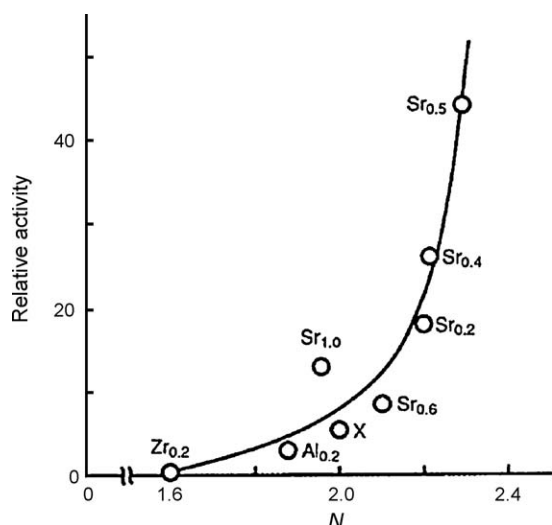


Fig. 3. Dependence of NO decomposition relative activity (specific surface area, m^2/g , was taken into account) on the average oxidation number (N) of copper in $\text{La}_{1-x}\text{A}_x\text{Cu}_{1-y}\text{B}_y\text{O}_3$ [22].

experiment (see Fig. 4b) proves that the existence of BaCO_3 is helpful for NO_x adsorption, ensuring the supply of NO_x to the reaction, which thus leads to the increase of the activity.

The above cases indicate that the substitution of A-site cations affect the reaction by changing the physicochemical properties of the catalyst or by enhancing the adsorption ability to NO_x species, but still the A-site cations were considered to be catalytically inactive and did not participate in the reaction scheme. However, this assumption just holds for A-site cations with permanent

oxidation states. In case that an A-site cation with variable oxidation state is introduced, the situation can change, since then it also has the ability to release or receive electrons depending on the reaction environment.

Indeed, it was reported [13] that the substitution of Ce for La in $\text{La}_{1-x}\text{Ce}_x\text{SrNiO}_4$ could further enhance the activity of NO decomposition (vs. $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$), and a high specific activity ($r = 2.6 \mu\text{mol s}^{-1} \text{m}^{-2}$ in 1% O_2 at 850 °C) could be shown even in the presence of oxygen. Because the influence on the oxidation state of B-site cations or on the amount of non-stoichiometric oxygen is not the only effect of Ce substitution (these two parameters could be achieved by Sr substitution alone), the enhanced activity thus suggests that Ce also participate in the reaction scheme. Considering the well-known property of ceria for oxygen storage/release, a new and complex active site for NO decomposition was proposed, in which the A'-site cation (i.e. Ce) is involved, accelerating the oxygen mobility, as shown in Fig. 5. This can be explained by the fact that Ce^{3+} has the possibility to supply one electron to $\text{Ni}^{3+}-\text{O}-\text{Ni}^{3+}$ forming Ce^{4+} , resulting in the easier removal of oxygen from $\text{Ni}^{3+}-\text{O}-\text{Ni}^{3+}$ to form $\text{Ni}^{3+}-[\text{O}]-\text{Ni}^{2+}$, i.e. the regeneration of the active site. This result indicate that the A-site cations are not by all means catalytically inactive, but that A-site cations indeed can participate in the reaction scheme as long as they possess an variable oxidation state.

Notably, the amount of Ce entering the structure frame of $\text{La}_{1-x}\text{Ce}_x\text{SrNiO}_4$ can reach up to 30% ($x = 0.3$), which is far higher than that reported for perovskite oxides with ABO_3 structure [24–26] (usually less than 10% for $\text{La}_{1-x}\text{A}'_x\text{BO}_3$). Belessi et al. [25] reported that the substitution of Ce in $\text{La}_{0.5}\text{Sr}_x\text{Ce}_y\text{FeO}_z$ is very difficult and actually Ce-containing perovskite oxides were not detected in this system. Zhao et al. [26] recently showed clear

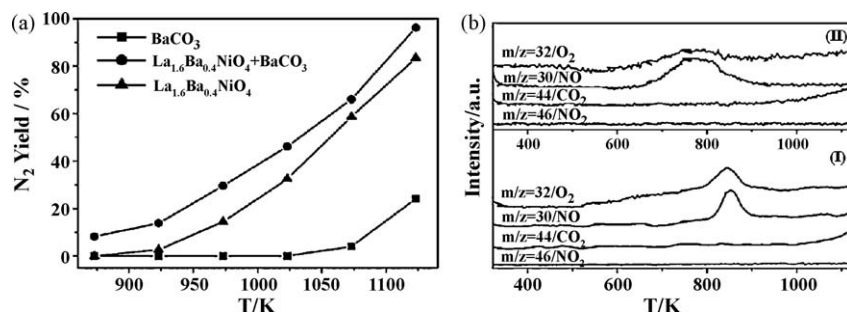


Fig. 4. (a) N_2 yield obtained from NO decomposition carried out over BaCO_3 , $\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_4$ and $\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_4/\text{BaCO}_3$ at various temperatures; (b) NO_2 -TPD profiles obtained from (I) BaCO_3 and (II) $\text{La}_{1.2}\text{Ba}_{0.8}\text{NiO}_4$ [23].

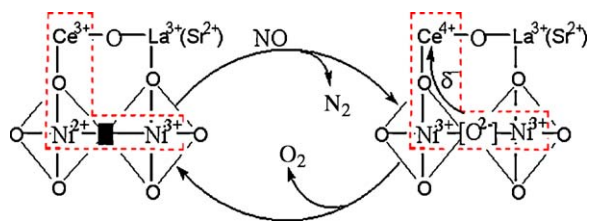


Fig. 5. A proposed active site structure of $\text{La}_{1-x}\text{Ce}_x\text{SrNiO}_4$ for NO decomposition (■ represents the oxygen vacancy) [13].

evidence from XRD patterns that CeO_2 phase appears when the amount of Ce in $\text{La}_{1-x}\text{Ce}_x\text{NiO}_3$ is above 5% ($x > 0.05$).

The reason that a higher amount of Ce could enter the structure of A_2BO_4 than ABO_3 might be that (1) there exists an alternate layer of AO in A_2BO_4 and, (2) there are more low-valence cations in A_2BO_4 (i.e. $x = 1$ of Sr^{2+} in $\text{La}_{2-2x}\text{Sr}_x\text{NiO}_4$) which facilitates the entry of high-valence cations (i.e. Ce^{4+}) to the framework to preserve electroneutrality. Hence, it is suggested that in order to fully use the virtues of Ce for oxygen storage/release, oxide catalysts with A_2BO_4 structure, rather than ABO_3 one, should be preferred, since the release of oxygen from the catalyst surface is recognized as a crucial step for catalytic NO removal carried out on perovskite-type catalyst.

Besides the above-mentioned effects, it was also suggested that the substitution of A-site cations sometimes could change the crystal phase from an ordered structure to a disordered one, and hence affects the catalytic performance. For example, Shin et al. [27] reported that $\text{Ca}_2\text{Fe}_2\text{O}_{5+\delta}$ with an ordered oxygen vacancy showed no activity for NO decomposition even at 900 °C, but high activity could be obtained after the substitution of Sr for Ca, i.e. $\text{Sr}_2\text{Fe}_2\text{O}_{5+\delta}$, in which disordered oxygen vacancies are present.

4. Effect of B-site substitution

The effect of the substitution of B-site cations is more complex than that of A-site cations, since the B-site cation not only exhibits a variable oxidation state, but also is one component of the active site. Simply, in case of $\text{AB}_{1-x}\text{B}'_x\text{O}_3$, the redox couple could be $\text{B}^{n+}/\text{B}^{(n-1)+}$ and/or $\text{B}^{n+}/\text{B}^{(n-1)+}$, and it is difficult (no direct evidence) to differentiate which couple plays the leading function. At present, the specification of the redox couple is just made empirical, that is, if high activity is obtained at a high amount of B' cation (i.e. $x > 0.5$), it is concluded that the $\text{B}^{n+}/\text{B}^{(n-1)+}$ couple plays the leading role in the catalytic reaction. Otherwise, the $\text{B}^{n+}/\text{B}^{(n-1)+}$ couple predominates the reaction. Of course, the case will be largely simplified if the B' cation just exists in a permanent oxidation state (e.g. Mg^{2+} ,

Al^{3+}). At this situation, $\text{B}^{n+}/\text{B}^{(n-1)+}$ is the only redox couple and the role of the B' cation is just to tune the oxidation state of B cation and/or the amount of non-stoichiometric oxygen.

However, the catalytic performance of B-site substituted sample has no relation to whether the oxidation state of B' cation is variable or not. Sometimes the B' cation with a permanent oxidation state leads to high activity, sometimes to a low one. Ishihara and co-workers [28] recently investigated the effect of B-site substitution on the activity of $\text{BaMn}_{1-x}\text{B}'_x\text{O}_3$ for NO decomposition, finding that the substitution with Mg leads to an increasing activity, while Cr and Cu leads to a decreasing activity. The substitution effect was found to follow the series $\text{Mg} > \text{Zr} > \text{Fe} > \text{Ni} > \text{Sn} > \text{Ta} > \text{Co} > \text{Cr} > \text{Cu}$. In case of $\text{LaSrNi}_{1-x}\text{B}'_x\text{O}_4$, the substitution effect by Al^{3+} (with the best conversion of 76%) however is weaker than that by Mn^{2+} (with the best conversion of 83%) [12,29]. Besides, it should be noted that a B'-site cation with a non variable oxidation state (e.g. Mg^{2+} , Al^{3+}) is usually difficult to be incorporated into the perovskite framework to a large amount.

Also, it has been reported that the substitution of B-site cations leads to a change of the Fermi level, which could be shown by plotting the temperature difference (ΔT) of the reduction peaks measured in H_2 -TPR experiment [30]. The effect of the Fermi level on NO decomposition and on NO reduction is however different: for NO decomposition without reductant, a higher Fermi level leads to high activity; while for NO reduction where a reductant is present, a lower Fermi level benefits the reaction to proceed [29,30]. This effect is summarized in Fig. 6.

Another interesting case is the substitution of the B-site cation by a noble metal (e.g. Pd). It is known that for a supported noble catalyst, the noble metal is prone to aggregation especially at higher temperatures. However, for perovskite oxides with their stable structures, the noble metal could endure temperatures as high as 900 °C without aggregation. More interestingly, the noble metal could go in and out the perovskite frame during the reaction process, in a form of $\text{Pd}^{2+} \leftrightarrow \text{PdO}$ [31]. As a result, this kind of catalysts (e.g. $\text{LaFe}_{0.57}\text{Co}_{0.38}\text{Pd}_{0.05}\text{O}_3$) can exhibit high activity for exhaust removal with a longer catalyst lifetime observed for a supported catalyst (see Fig. 7), thus coupling the advantages of noble metal (e.g. excellent catalytic performance) with these of perovskite oxides (e.g. high thermal stability).

5. Perovskite-type oxides as catalyst or catalyst support

Like most simple oxidic catalysts (e.g. CuO/CeO_2), perovskite-type catalysts were also investigated either as a "support" (e.g. $\text{Pt}/\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$) or as an "active phase" supported on another oxide (e.g. $\text{La}_2\text{NiO}_4/\text{ZrO}_2$), in order to fully exploit their catalytic

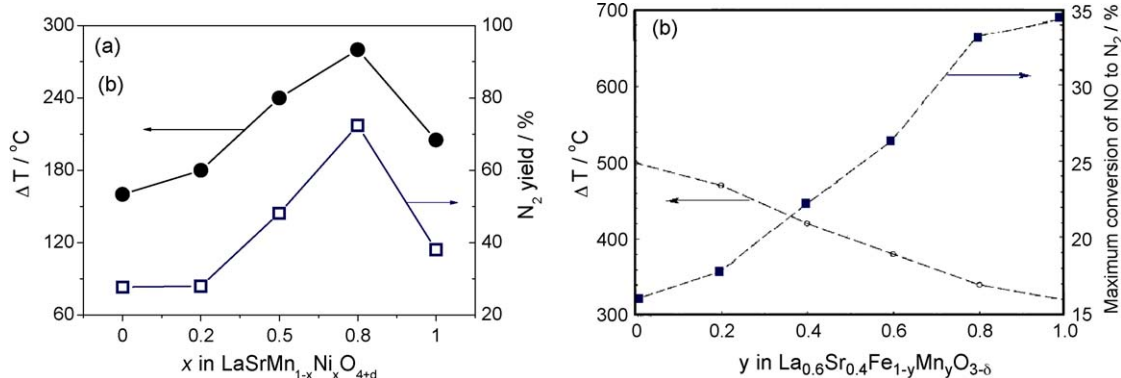


Fig. 6. Relationships between the difference in temperature (ΔT) and NO removal activity: (a) NO decomposition on $\text{LaSrMn}_{1-x}\text{Ni}_x\text{O}_{4+\delta}$ in the presence of 2.5 v/v% O_2 at 850 °C [29]; (b) Maximum conversion of NO to N_2 ($\text{C}_2\text{H}_6 + \text{O}_2 + \text{NO}$) over $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{1-y}\text{Mn}_y\text{O}_{3-\delta}$ [30].

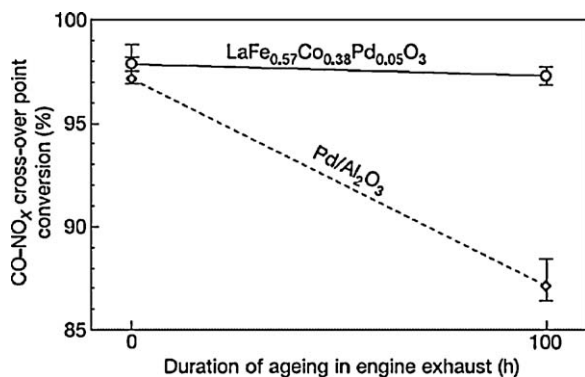


Fig. 7. Dependence of the CO-NO_x cross-over point conversion on the reaction time over Pd containing perovskite catalyst, LaFe_{0.57}Co_{0.38}Pd_{0.05}O₃, and Pd supported catalyst, Pd/γ-Al₂O₃ [31].

performance for NO removal. These catalysts were usually prepared by an impregnation method.

Biniwale et al. [32] investigated and compared the catalytic performance of La_{0.7}Sr_{0.3}MnO₃, 0.1 wt.% Pt/La_{0.7}Sr_{0.3}MnO₃ and La_{0.7}Sr_{0.3}Mn_{0.97}Pt_{0.03}O₃ (that is a catalytic system without Pt, one with supported Pt and one with Pt within the framework) for NO reduction by H₂, finding that the activation of NO and H₂ is more favorable on 0.1 wt.% Pt/La_{0.7}Sr_{0.3}MnO₃, which showed the best activity for NO reduction (see Table 1). It was concluded that Pt could be stabilized when loaded on perovskite-type oxides while the B-site cation of perovskite still takes part in the reaction as an active site. Liu et al. [33] also reported that the doping of Ag on perovskite-type oxides largely improved the activity for NO removal, and concluded that some of Ag⁺ cations occupied the La³⁺ site, which subsequently affects the physicochemical properties of the sample and hence, the catalytic performances. Notably they pointed out that (1) the presence of oxygen is absolutely necessary for NO decomposition and, (2) inhibition of SO₂ and H₂O is largely mitigated after the doping of Ag.

In case that perovskite-type oxide was used as supported “active phase”, as precursors usually the corresponding metal nitrates or citrates were used [34]. Also, the impregnation of the synthesized perovskite-type oxides directly on the support has been reported (in this case, the perovskite-type oxides were first grinded in aqueous solution, then loaded on the support and finally dried at desired temperature), but the catalytic performance of sample prepared by this way can be even poorer than that of the bulk perovskite. Indeed, it was found in a previous experiment that the catalytic activity of LaSrNiO₄/MgO for NO decomposition is lower than for LaSrNiO₄ alone [35].

It should be however noted that the type of perovskite formed on the surface depends closely on the support. Pomonis et al. [34] investigated the La-Ni-O oxides formed on Al₂O₃ and ZrO₂ supports, finding that the crystal phase developed on ZrO₂ is La₂NiO₄, while that on Al₂O₃ is LaNiO₃. Of course, the catalytic performance of these systems for NO removal was therefore different, in order of La₂NiO₄/ZrO₂ > LaNiO₃/Al₂O₃. The reason is that there is a stronger affinity between O and Ni³⁺ in the latter case, making the desorption of oxygen (*i.e.* regeneration of the active site) difficult and hence, resulting in a lower activity.

Table 1

Temperature-programmed reaction of NO reduction by H₂ over various catalysts [32].

Catalyst composition	Conversion ^a (%)	N ₂ selectivity ^a (%)	NH ₃ selectivity ^a (%)	TOF ^a (10 ⁻³ min ⁻¹)
La _{0.7} Sr _{0.3} MnO ₃	99.1	38.38	61.7	15.0
0.1 wt.%Pt/La _{0.7} Sr _{0.3} MnO ₃	99.6	63.26	36.7	21.1
La _{0.7} Sr _{0.3} Mn _{0.97} Pt _{0.03} O ₃	99.5	52.64	47.9	20.4

^a This value was estimated at equilibrium state of the reaction at 900 °C.

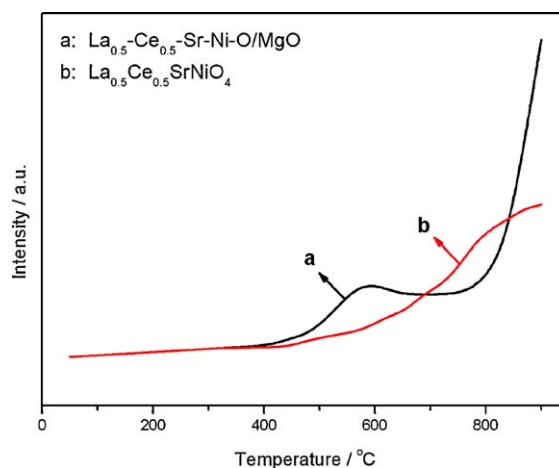


Fig. 8. O₂-TPD profiles obtained from the “pure” (La_{0.5}Ce_{0.5}SrNiO₄) and supported (La_{0.5}-Ce_{0.5}-Sr-Ni-O/MgO) perovskite-type catalysts [36].

The effect of incorporated Ce on the catalytic performance of LaSrNiO₄ using MgO as support has been studied recently for NO decomposition [36]. It was found that although perovskite-type oxides with not well defined structure were formed at this time, the sample La_{0.5}-Ce_{0.5}-Ni-O/MgO showed high activity for NO decomposition. The reason was suggested to be the formation of a new, yet unknown, active site, which benefits the oxygen desorption from the catalyst surface, as supported by O₂-TPD experiment (Fig. 8). It was observed that the temperature and the amount of oxygen desorbed from La_{0.5}-Ce_{0.5}-Sr-Ni-O/MgO are totally different from these from La_{0.5}Ce_{0.5}SrNiO₄, indicating a different active site for oxygen desorption.

In summary, the modification of perovskite-type catalysts, either being taken as a support or as an active phase, can be advantageous for improving its catalytic performance for NO removal, even though no definite rules for beneficial or detrimental effects of the modification could so far be established. Although pure perovskite-type catalysts are convenient for the study of the relationship between structure properties and catalytic performance, such a supported perovskite-type catalyst could be preferred in practical application, due to the possibility of increasing its activity by simple preparation methods.

6. Relationship between electrochemical properties and catalytic performances

Traditional characterization methods for perovskite-type oxides, such as O₂-TPD and XPS, have been largely reported in the literatures, and it is straightforward to find the relationships between them and the catalytic performance of the respected catalyst. Therefore, the properties originated from these characterization methods are not discussed in this review, and the effort made here concentrates mainly on the relations between electrochemical properties and catalytic performances.

A redox catalytic reaction can be roughly divided into two steps: oxidation (*i.e.* electron donation) and reduction (*i.e.* electron reception). This means that the catalyst should have the ability for both, reduction and oxidation, or at least another reactant or

Table 2

Electrochemical properties and catalytic performances of various catalysts for NO direct decomposition [10].

Catalysts	NO conv. ^a (%)	NO conv. ^b (%)	R. P. A. ^c (a.u.)	Red. pot. ^d (V)	Ox. pot. ^e (V)	ΔE^f (V)
La ₂ CuO ₄	1.0	1.9	5	2.49	3.35	0.86
La _{1.5} Sr _{0.5} CuO ₄	60.0	9.8	40	2.0	2.9	0.9
LaSrCuO ₄	96.8	34.3	188	1.30	3.13	1.77
LaSrCoO ₄	39.9	20.3	–	–	2.15	–
LaSrNiO ₄	80.1	94.7	22	2.75	3.25	0.5

^a NO conversion obtained from NO + CO reduction reaction at 400 °C.^b NO conversion obtained from NO direct decomposition at 850 °C.^c R. P. A. = redox peak area.^d Red. pot. = reductive potential.^e Ox. pot. = oxidative potential.^f ΔE = the difference in oxidative and reductive potentials.

assistant (e.g. reducing agent) has to be present to support the redox cycle of catalyst to proceed. That is, the redox ability of a catalyst should be a crucial parameter in deciding its activity for a catalytic reaction. The higher the symmetry of the redox potentials is, the quicker the catalytic cycle proceeds. However, the characterization of heterogeneous catalyst for NO decomposition by electrochemical methods is still in its infancy, even though lately some works have been done regarding this topic. [10,29,37–39].

Two methods might be used for characterizing the electrochemical properties of a catalyst. One is the direct measurement by cyclic voltammetry (CV), giving the symmetry of redox potentials (which represents the redox ability) and the redox peak area (which represents the amount of active site). For example, the electrochemical parameters of several catalysts by a CV method was measured, and compared to the activity for NO reduction and NO decomposition, finding that for NO reduction (by CO), the activity depends mainly on the redox area of catalyst, while for NO decomposition, the symmetry of redox potentials plays the crucial role (see Table 2) [10].

For NO reduction, the apparent redox potentials of the catalyst, according to the Nernst Equation, would be reduced due to the presence of reducing agent (e.g. CO), thus the role of the symmetry of redox potentials becomes weak in the reaction since the redox cycle of catalyst could proceed easily with the aid of reducing agent. As a result, the area of the redox peak, which represents the amount of active site, predominates in the reaction and hence, sample LaSrCuO₄ with the largest redox peak area showed the best activity for NO reduction (by CO).

For NO decomposition, however, the difference in redox potentials will be enlarged (NO is an oxidant) and the proceeding of the redox reaction on the catalyst becomes difficult. As a result, the symmetry of redox potentials become the crucial parameter in deciding the catalytic reaction and thus, LaSrNiO₄ with the smallest difference in redox potentials showed the best activity for NO decomposition.

It can be concluded that a crucial pre-requisite for the catalytic reaction to occur is that the full redox cycle can proceed easily. Thus only when this requirement is fulfilled, other parameters, such as the amount of active sites, should come into the focus of the catalyst design. Fig. 9 represents the change of redox potentials under an oxidative and reductive atmosphere. This shows the importance of reducing agent in changing the apparent redox potentials of the catalyst.

The limitation of this method is that the CV measurement is usually carried out at room temperature, which is not a practical condition for catalytic reactions, which indeed is normally carried out at higher temperature. Still it should be applicable for catalyst characterization, since the difference in redox potentials in the Nernst Equation simply relates to the reaction temperature (T).

Another method for measuring the electrochemical properties of a catalyst is the temperature programmed reduction of hydrogen (H₂-TPR). H₂-TPR is an efficient measurement for characterizing the redox ability of solid state catalysts in heterogeneous catalysis. However, no relationship between the H₂-TPR and the electrochemical properties of a catalyst has been proposed yet. It was until recently proposed that the symmetry of redox potentials (ΔE) could be represented by the reduction peak areas: $\Delta E = (RT/nF) \cdot \ln(A_F/A_S)$, where A_F and A_S represent the first and second reduction peak area, respectively [29].

The results shown in Fig. 10 indicate that the ΔE (calculated from H₂-TPR experiment) indeed has a close relation to the NO decomposition activity, and hence it is suggested that this method could be an indication in predicting the catalytic performance of catalyst for NO decomposition.

7. Active site structure and reaction mechanism

The search for the structure of the active site in oxide catalyst for NO removal could be traced back to literatures published in 1971, where it was reported that a surface R₂-center (which are pairs of adjacent oxygen vacancies with one electron (F⁺ centers))

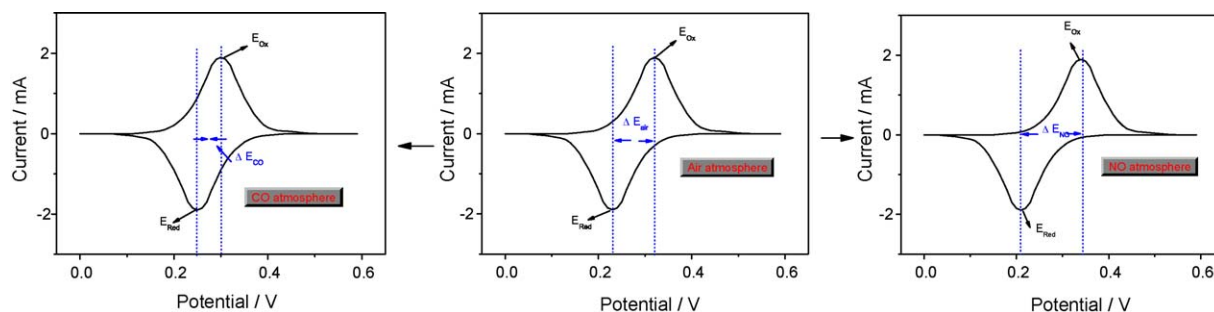


Fig. 9. A schematic profile for the change of redox potentials in oxidative (e.g. NO) and reductive (e.g. CO) atmosphere. Here the change of the profiles in different atmospheres were speculated based on the Nernst Equation.

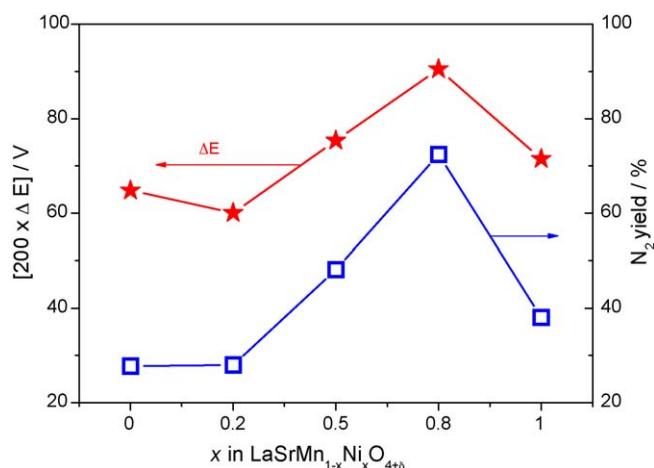
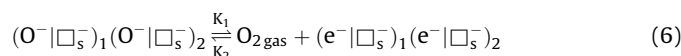
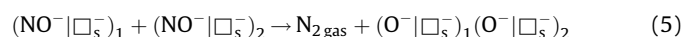
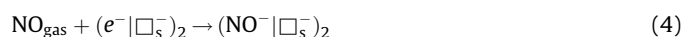
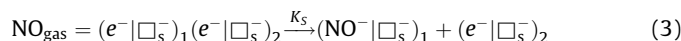


Fig. 10. Relationships between the difference in redox potentials (ΔE) and N_2 decomposition activity (in 2.5 v/v% O_2 , at 850 °C) of $\text{LaSrMn}_{1-x}\text{Ni}_x\text{O}_{4+\delta}$ [29].

is the active site for NO decomposition in ordinary metal oxides, and O_2 -desorption (see reaction (6)) is the rate-determining step [40], as shown below:



At the beginning, one gaseous NO molecule attacks a surface electronegative vacancy, to form an activated state “ NO^- ” accepting one electron. After that, two activated NO molecules collide with each other and a stable $\text{N}\equiv\text{N}$ bond is formed stepwise. Finally, the N_2 molecule desorbs and the two remaining oxygen atoms collide to form the O_2 molecule, which will escape the catalyst surface when enough energy is offered, accompanied by the regeneration of the oxygen vacancy.

Later, Shin et al. [41] investigated the NO decomposition activity over SrFeO_{3-x} and, based on results of IR measurements proposed that NO adsorbs on perovskite is in form of NO^- and that the active site contains two adjacent oxygen vacancies (see Fig. 11).

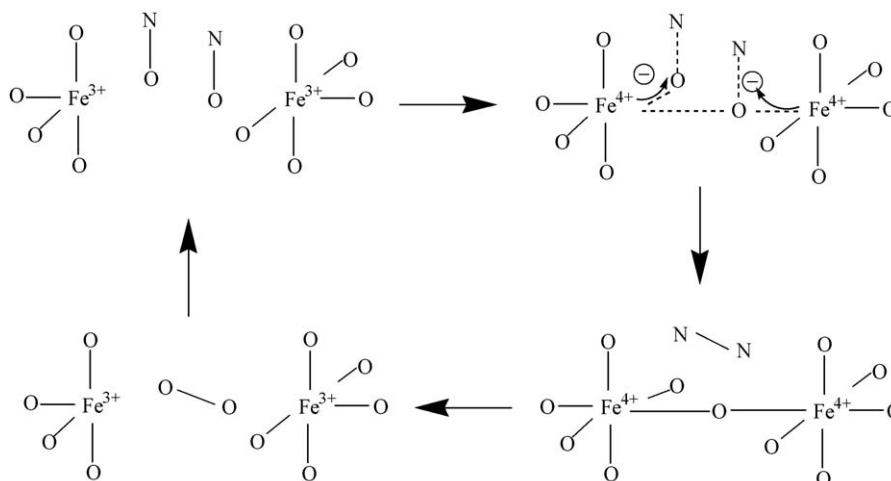


Fig. 11. Possible mechanism of NO decomposition on perovskite-type catalyst, proposed by Shin et al. [41].

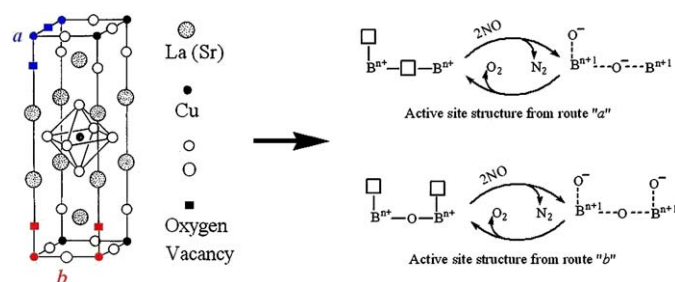


Fig. 12. Two proposed active site structures for NO decomposition reaction carried out on perovskite-type catalyst. Model *a* was proposed by Shin et al. [41]; model *b* by Zhu et al. [12].

The above proposed active site structure of NO decomposition was generally accepted in the following publications. However, later it was suggested that the active sites for NO decomposition are composed of two oxygen vacancies, two transition metals, and one lattice-oxygen, with the oxygen vacancy located on the apex of the MO_6 octahedron and the lattice oxygen locating between the two transition metals (i.e., $\text{M}-\text{O}-\text{M}$ plane), as shown in Fig. 12. This assumption was based on the NO decomposition activity over LaSrCuO_4 with *T* and *T'* phase (in which the local $\text{Cu}-\text{O}$ unit is an octahedron and a pyramid, respectively) is different and the activation energy of oxygen desorption is different depending on the form of the oxygen vacancy (by DFT calculation) [12]. This new structure (route “*b*” in Fig. 12) seems reasonable since it involves the participation of the lattice oxygen, which is recognized to be an important criterion in judging the NO decomposition activity.

The reaction mechanism of NO reduction is variable depending on the reducing agent used, and even for a certain reducing agent, there may be several reaction mechanisms. Therefore, the reaction mechanism of NO reduction is not going to be discussed in this small review, and what mentioned here mainly is the mechanism of NO decomposition.

For the mechanism of NO decomposition on perovskite-type catalyst, pioneering works of Shin et al. [41] considered that at the beginning of the reaction, two NO molecules attack two adjacent oxygen vacancies *simultaneously*, and after the adsorption and activation steps, the two activated nitrogen atoms and subsequently, the two left oxygen atoms combine with each other to form the N_2 and O_2 molecules (see Fig. 11), as the mechanism proposed for metal oxides.

Teraoka et al. [9] studied the kinetics of NO decomposition carried out on Co- and Mn-based perovskite-type oxides and found

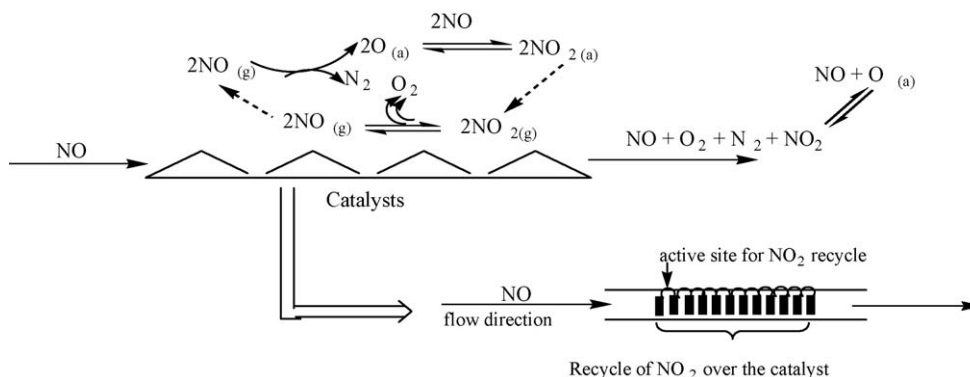
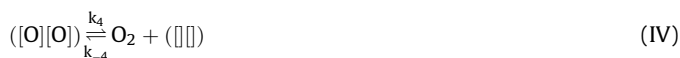
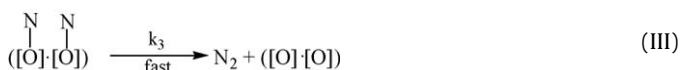
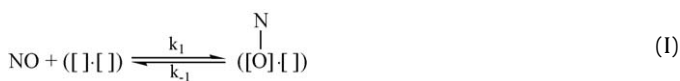


Fig. 13. Recycle mechanism proposed for NO decomposition reaction carried out on perovskite-type catalyst [11].

that the reaction order of NO in the reaction is 1. As a result, they suggested that the attack of NO on the oxygen vacancy occurred stepwise, and the attack of the second NO molecule is considered to be the rate-determining step, described as follows:



Although some other steps, such as NO₂ formation, N₂O formation and decomposition, etc. were also considered in the updating works, the opinion that the formation of N₂ is directly caused from the collision of two activated nitrogen atoms and the formation of O₂ is combined by the two left oxygen atoms, has not changed afterwards.

An alternative mechanism of NO decomposition was proposed lately [11]. It is known that in NO decomposition, the amount of O₂ detected is always lower than that of N₂ due to the formation of NO₂ (2NO + O₂ = 2NO₂), whereas no study regarding the way of NO₂ formation has been carried out in previous reports. An investigation on the way of NO₂ and O₂ formation however showed that (1) the formation of NO₂ proceeds mainly on the catalyst surface (i.e. NO + O_(a) = NO₂) and, (2) the oxygen desorption step (O_(a) + O_(a) = O₂) is not the preferred way of O₂ formation in the NO decomposition reaction. As a result, it was proposed that the mechanism of NO decomposition is through the circulatory dissociation of NO₂, as shown in Fig. 13. An indication for this assumption is that NO₂ species could be observed in NO-TPD experiment, in which the gaseous oxygen is not present, namely, NO₂ could be formed through the reaction of NO + O_(a) = NO₂.

8. Conclusions

Perovskite-type oxides are promising catalysts for NO removal. Their high activity accompanied with low cost makes them a potential candidate for industrial application. Therefore, finding a highly efficient perovskite-type catalyst for NO removal would be a subject of great interest.

This review outlined the relationship of structural and physicochemical properties, as well as electrochemical properties,

on the catalytic performances of perovskite-type catalyst for NO removal. The former indicates that certain modifications of the catalyst can be beneficial for improving its catalytic activity; while the latter suggests that the electrochemical characterization would be a potential and powerful method for selecting an active catalyst. Also, the active site and reaction mechanism for NO decomposition proposed in the literatures are discussed and compared. Although these mechanisms are still a matter of debate, a common point is that the active site should allow the oxygen atoms to combine on the surface easily, and thus that the desorption of oxygen from the catalyst surface is a very important step of the reaction.

Using the current knowledge on the effect of structure and composition of perovskites on their catalytic activity as well as the analytical tools presented in this review, it can be at least hoped that the search for an efficient perovskite catalyst for NO removal, fulfilling the requirements for large scale applications will finally be successful.

References

- [1] M. Bowker, Chem. Soc. Rev. 37 (2008) 2204–2211.
- [2] V.I. Parvulescu, P. Grange, B. Delmon, Catal. Today 46 (1998) 233–316.
- [3] O. Kubaschewski, C.B. Alcock, P.J. Spencer, Materials Thermochemistry, 6th ed., Pergamon Press, Oxford, 1993.
- [4] M. Iwamoto, H. Furukawa, Y. Mine, F. Uemura, S.I. Mikuriya, S. Kagawa, J. Chem. Soc. Chem. Commun. (1986) 1272–1273.
- [5] G. Spoto, A. Zecchina, S. Bordiga, G. Ricchiardi, G. Martra, G. Leofanti, G. Petrini, Appl. Catal. B-Environ. 3 (1994) 151–172.
- [6] C.N. Costa, A.M. Efstathiou, J. Phys. Chem. C 111 (2007) 3010–3020.
- [7] D.I. Kondarides, T. Chafik, X.E. Verykios, J. Catal. 191 (2000) 147–164.
- [8] J. Liu, Z. Zhao, C.M. Xu, A.J. Duan, Appl. Catal. B-Environ. 78 (2008) 61–72.
- [9] Y. Teraoka, T. Harada, S. Kagawa, J. Chem. Soc. Faraday Trans 94 (1998) 1887–1891.
- [10] J.J. Zhu, Z. Zhao, D. Xiao, J. Li, X.G. Yang, Y. Wu, Electrochem. Commun. 7 (2005) 58–61.
- [11] J.J. Zhu, D.H. Mao, J. Li, X.F. Xie, X.G. Yang, Y. Wu, J. Mol. Catal. A-Chem. 233 (2005) 29–34.
- [12] J.J. Zhu, X.G. Yang, X.L. Xu, K.M. Wei, J. Phys. Chem. C 111 (2007) 1487–1490.
- [13] J.J. Zhu, D.H. Xiao, J. Li, X.G. Yang, Y. Wu, J. Mol. Catal. A-Chem. 234 (2005) 99–105.
- [14] J. Liu, Z. Zhao, C.M. Xu, A.J. Duan, G.Y. Jiang, J. Phys. Chem. C 112 (2008) 5930–5941.
- [15] H. Wang, Z. Zhao, P. Liang, C.M. Xu, A.J. Duan, G.Y. Jiang, J. Xu, J. Liu, Catal. Lett. 124 (2008) 91–99.
- [16] J. Liu, Z. Zhao, C.M. Xu, A.J. Duan, T. Meng, X.J. Bao, Catal. Today 119 (2007) 267–272.
- [17] R.J.H. Voorhoeve, Advanced Materials in Catalysis, Academic Press, New York, 1977.
- [18] M.A. Pena, J.L.G. Fierro, Chem. Rev. 101 (2001) 1981–2017.
- [19] V.M. Goldschmidt, Skr. Nor. Videnk. -Akad., K1. I: Mater. Naturvidensk K1., 1926.
- [20] Z. Zhao, X.G. Yang, Y. Wu, Appl. Catal. B-Environ. 8 (1996) 281–297.
- [21] J.J. Zhu, X.G. Yang, X.L. Xu, K.M. Wei, Sci. China Ser. B 50 (2007) 41–46.
- [22] H. Yasuda, N. Mizuno, M. Misono, J. Chem. Soc. Chem. Commun. (1990) 1094–1096.
- [23] Y.J. Zhu, D. Wang, F.L. Yuan, G. Zhang, H.G. Fu, Appl. Catal. B-Environ. 82 (2008) 255–263.
- [24] J. Kirchnerova, M. Alifanti, B. Delmon, Appl. Catal. A-gen. 231 (2002) 65–80.
- [25] V.C. Belessi, C.N. Costa, T.V. Bakas, T. Anastasiadou, P.J. Pomonis, A.M. Efstathiou, Catal. Today 59 (2000) 347–363.
- [26] B. Zhao, R. Wang, X.X. Yang, Catal. Commun. 10 (2009) 1029–1033.

- [27] S. Shin, Y. Hatakeyama, K. Ogawa, K.Y. Shimomura, *Mater. Res. Bull.* 14 (1979) 133–136.
- [28] H. Iwakuni, Y. Shinmyou, H. Yano, H. Matsumoto, T. Ishihara, *Appl. Catal. B-Environ.* 74 (2007) 299–306.
- [29] J.J. Zhu, D.H. Xiao, J. Li, X.G. Yang, *Catal. Lett.* 129 (2009) 240–246.
- [30] K.K. Hansen, E.M. Skou, H. Christensen, T. Turek, *J. Catal.* 199 (2001) 132–140.
- [31] Y. Nishihata, J. Mizuki, T. Akao, H. Tanaka, M. Uenishi, M. Kimura, T. Okamoto, N. Hamada, *Nature* 418 (2002) 164–167.
- [32] R.B. Biniwale, J.V. Pande, M. Dhakad, N.K. Labhsetwar, M. Ichikawa, *Catal. Lett.* 123 (2008) 164–171.
- [33] Z.M. Liu, J.M. Hao, L.X. Fu, T.L. Zhu, *Appl. Catal. B-Environ.* 44 (2003) 355–370.
- [34] A.K. Ladavos, P.J. Pomonis, *Appl. Catal. B-Environ.* 2 (1993) 27–47.
- [35] J. Zhu, D. Xiao, J. Li, X.G. Yang, Y. Wu, Unpublished.
- [36] J.J. Zhu, D.H. Xiao, J. Li, X.G. Yang, K.M. Wei, *Catal. Commun.* 7 (2006) 432–435.
- [37] J.J. Zhu, X.G. Yang, X.L. Xu, K.M. Wei, *Chinese Sci. Bull.* 51 (2006) 374–376.
- [38] J.J. Zhu, Z. Zhao, D.H. Xiao, J. Li, X.G. Yang, Y. Wu, *J. Mol. Catal. A-Chem.* 238 (2005) 35–40.
- [39] L. Li, Y.Y. Zhan, Q. Zheng, Y.H. Zheng, X.Y. Lin, D.L. Li, J.J. Zhu, *Catal. Lett.* 118 (2007) 91–97.
- [40] E.R.S. Winter, *J. Catal.* 22 (1971) 158–170.
- [41] S. Shin, H. Arakawa, Y. Hatakeyama, K. Ogawa, K. Shimomura, *Mater. Res. Bull.* 14 (1979) 633–639.